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H. E. French

The Preparation of Substituted Alpha Halogen Benzyl Benzoates

THE PREPARATION OF SUBSTITUTED ALPHA HALOGEN BENZYL BENZOATES, AND A STUDY OF THE REACTIONS OF THESE COMPOUNDS

BY

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Herbert Ephraim French

ENTITLED THE PREPARATION OF SUBSTITUTED ALPHA HALOGEN BENZYL BENZOATES, AND A STUDY OF THE REACTIONS OF THESE COMPOUNDS.

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A C K N O W L E D G M E N T

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I. INTRODUCTION

The aldehydes are among the compounds whose reactions have been most extensively studied, therefore it is surprising that their behavior with acid halides has received so little attention. Since 1857, when the first paper on that reaction appeared, a number of investigators have touched upon this problem, but no very extensive study of it was made. The investigation was confined almost entirely to the alifatic series, and several condensations were made by the action of various acid halides on formaldehyde, acetaldehyde, and their polymers, showing that the reaction is a general one for those two aldehydes. The structure of the addition product was proved and a few of its reactions were noted. In the aromatic series practically no work was done. Benzoyl chloride and benzoyl bromide were found to react with benzaldehyde but the structures of the products were not worked out, and no study was made of the properties and reactions of the substances formed.

In this laboratory, this problem has been the subject of considerable investigation with the purpose of finding whether the reaction is a general one for all aldehydes and acid halides, to prove the structures of the substances formed, and to study the ease of formation, stability, and reactions of the products. In the first paper on this work[23], the proof of the structures of the reaction products is given together with some general conclusions relative to the stability of those substances. The results of that work indicated that the reaction is a general one, although in several cases the products could not be isolated because of their instability.

The purpose of the present investigation, which has been confined to the aromatic series, has been first, to determine wheth-

er the reaction is a general one, and whether the unstable reaction products which cannot be isolated are simple addition products; and second, to study the ease of formation, stability, and reactions of the substances formed.

II. HISTORICAL

By the action of chlorine on acetaldehyde in a closed tube, Wurtz[1] obtained a liquid having the empirical formula $C_4H_7ClO_2$. He attributed its formation to the intermediate polymerization of the acetaldehyde, followed by the replacement of a hydrogen by a chlorine atom. Later, Simpson[2] obtained the same substance when he heated acetyl chloride and acetaldehyde together in a sealed tube. This led him to the belief that its formation from the action of chlorine in acetaldehyde was due to a preliminary formation of acetyl chloride which then reacted with the acetaldehyde. The corresponding bromine compound, $C_4H_7BrO_2$, was prepared by Tawildarow[3], by heating acetyl bromide and acetaldehyde in a sealed tube. Schiff[4] finally proved that the substance $C_4H_7ClO_2$ was α chlor ethyl acetate, $CH_3CHCl.O.CO.CH_3$, for on treatment with potassium acetate, it yielded ethylidene diacetate, a known compound[5]. Franchimont[6] found that the same addition compound could be prepared by heating acetyl chloride and paraldehyde together in a sealed tube. A number of analogous compounds were prepared by Rubencamp[7] by the action of different acid chlorides on acetaldehyde in closed tubes. The products of these reactions were treated with the silver salts of fatty acids and a series of ethylidene derivatives homologous to the ethylidene diacetate prepared by Schiff[4] were obtained. The following table represents Rubencamp's work:

Addition Product	B.P.	Treated with	Product Obtained	B.P.
acetaldehyde acetyl chloride	121.5°	silver acetate	ethylidene diacetate	168.4°
acetaldehyde acetyl chloride	121.5°	silver propion-ate	ethylidene acet-propionate	178.6°
acetaldehyde propionyl chlor-ide	135°	silver acetate	ethylidene propion-acetate	178.7°
acetaldehyde pripionyl chlor-ide	135°	silver propion-ate	ethylidene diprop-ionate	192.2°
acetaldehyde acetyl chloride	121.5°	silver butyrate	ethylidene acet-butyrate	192.4°
acetaldehyde butyryl chloride	149°	silver acetate	ethylidene butyr-acetate	192.8°
acetaldehyde butyryl chloride	149°	silver butyrate	ethylidene dibutryate	215.5°
acetaldehyde acetyl chloride	121.5°	silver valerate	ethylidene acet-valer-ate	194-199°
acetaldehyde valeryl chloride	162°	silver acetate	ethylidene valer-ace-tate	194-199°
acetaldehyde valeryl chloride	162°	silver valerate	ethylidene divalerate	225°

Henry[8] found that when polyoxymethylene was heated with acetyl chloride in a closed tube, the substance $CH_2Cl.O.CO.CH_3$ was produced. Acetyl bromide was found to react more readily than the acetyl chloride, yielding the corresponding bromine compound. These substances were unstable, and reacted readily with water, producing acetic acid, formaldehyde, and halogen acid.

The action of benzoyl chloride on the higher alifatic aldehydes and ketones was studied by Lees[9], who found that the reaction here was more complex, due to the tendency of the addition compound to lose halogen acid. In the case of ketones, halogen acid can be eliminated in two ways, but he was unable to determine which isomer was obtained. Thus, the condensation product of methyl n-nonyl ketone and benzoyl chloride split out hydrochloric acid and produced an unsaturated compound according to the reaction:

$$C_9H_{19}.CO.CH_3 + C_6H_5COCl \rightarrow C_8H_{17}CH_2\text{-}\underset{\underset{CH_2}{\|}}{C}\text{-}O.CO.C_6H_5 \qquad \text{or}$$

$$C_8H_{17}CH=\underset{\underset{CH_3}{|}}{C}\text{-}O\text{-}CO\text{-}C_6H_5 + HCl$$

Analogous reactions were obtained with benzoyl chloride and methyl n-butyl ketone, methyl sec. hexyl ketone, methyl n-heptyl ketone, acetophenone, camphor, and heptaldehyde. With the last three substances hydrochloric acid can split out in only one way, so that substances of known structure were obtained. The action of benzoyl chloride on acetone and on methyl n-propyl ketone was tested, but although the mixtures were refluxed for some time, there was no reaction. He explained this failure to react by saying that the boiling points of the mixtures were below the temperatures necessary for reaction to take place.

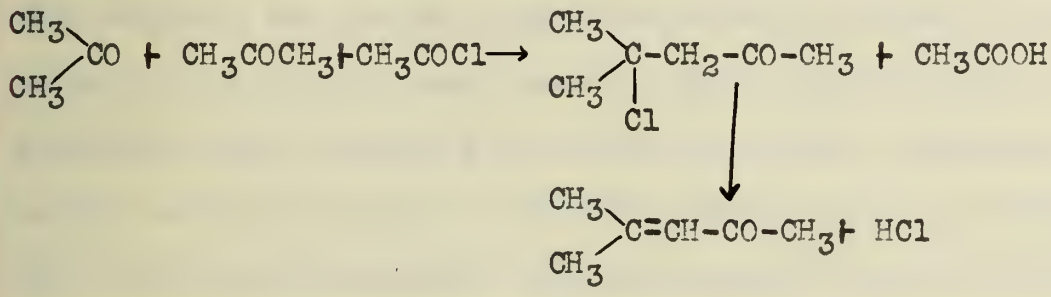
A study of the catalytic action of anhydrous zinc chlor-

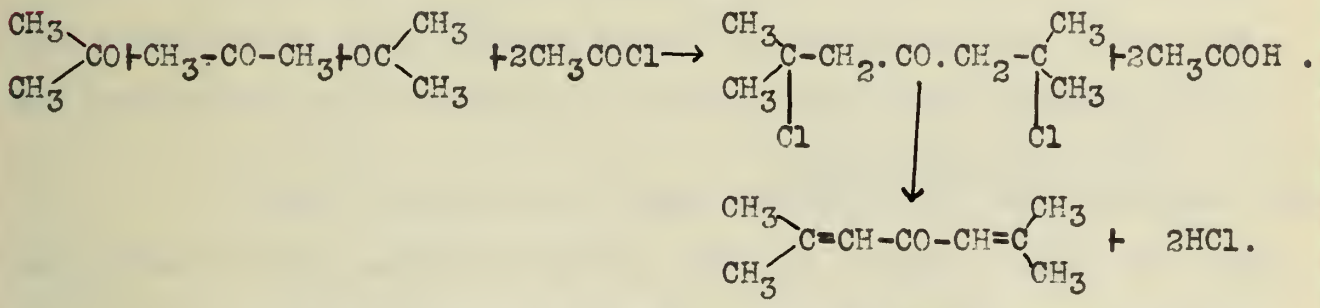
ide on the addition of acid halides to aldehydes was made by Descude[10] who found that it had a very decided effect in increasing the speed of the reaction. For example, Descude found that the addition of a small piece of anhydrous zinc chloride to a mixture of acetyl chloride and paraldehyde caused a vigorous reaction to take place at once, while Franchimont[6] heated the same mixture in a sealed tube in order to get a reaction. In the same way, a small piece of zinc chloride added to a mixture of polyoxymethylene and acetyl chloride caused an immediate reaction, whereas Henry[8] found it necessary to heat the two substances in a closed tube. Descude found the catalytic effect of zinc chloride was very great in reaction mixtures containing aromatic acid chlorides. Thus, benzoyl chloride had no action of polyoxymethylene when the two were refluxed together, but the addition of a small piece of anhydrous zinc chloride caused a very smooth reaction to take place at the temperature of a water bath.

A number of addition compounds of various aromatic and alifatic acid chlorides and polyoxymethylene were prepared by Descude. These products were then converted into methylene di-esters by heating them above 160° with the potassium salts of different acids. Descude's work is represented by the following table:

Addition Product	Treated With	Product Obtained
polyoxymethylene o-toluyl chloride	potassium o-toluate	methylene ditoluate (o)
polyoxymethylene m-toluyl chloride	potassium m-toluate	methylene ditoluate (m)
polyoxymethylene p-toluyl chloride	potassium p-toluate	methylene ditoluate (p)
polyoxymethylene propionyl chloride	potassium propionate	methylene dipropionate
polyoxymethylene isobutyryl chloride	potassium isobutyrate	methylene dibutyrate(iso)
polyoxymethylene n-butyryl chloride	potassium n-butyrate	methylene dibutyrate (n)
polyoxymethylene isovaleryl chloride	potassium iso valerate	methylene divalerate(iso)
polyoxymethylene n-valeryl chloride	potassium n-valerate	methylene divalerate (n)
polyoxymethylene phenyl acetyl chloride	potassium phenyl acetate	methylene diphenyl acetate

The action of acid chlorides on ketones in the presence of anhydrous zinc chloride was also investigated by Descude, who found that simple addition compounds were never formed. Thus, two moles of acetone and one of acetyl chloride reacted to give mesityl oxide, and if three moles of acetone were used, phorone was produced. The presence of the acid chloride was essential, and Descude explained its function as follows:





In the aromatic series, much less work has been done. Wöhler and Liebig[11], in 1832, obtained a semi-solid product from the action of bromine on benzaldehyde, which they believed was benzoyl bromide. Later, L. Claisen[12] prepared pure benzoyl bromide, and found that it reacted with benzaldehyde to give the same substance that Wöhler and Liebig had obtained. Claisen purified and analyzed his product and found its empirical formula to be $C_{14}H_{11}O_2Br$, and suggested the following as a possible structure: C_6H_5-CHBr-O-CO-C_6H_5.

The corresponding chlorine compound, $C_{14}H_{11}O_2Cl$, was prepared by Laurent and Gerhardt[13] by the action of chlorine on benzaldehyde. Schiff[14] showed that the same substance could be produced

by the action of benzoyl chloride on benzaldehyde.

Staudinger and Anthes[15] treated benzaldehyde with benzoyl iodide, in petrol ether solution, and obtained an unstable solid which they assumed to be iod benzyl benzoate. They made no investigation of the material, however.

The reactions of oxalyl chloride with aromatic aldehydes and ketones were studied by Staudinger and Anthes[15], who found that the aldehyde and ketone oxygen was always replaced by two chlorine atoms if the mixture were heated. With benzaldehyde and cinnamyl aldehyde, they were able to isolate addition products. The benzaldehyde addition compound was very unstable and decomposed readily, but the cinnamyl aldehyde addition product was sufficiently stable to permit its purification and analysis. It was found to contain two molecules of the aldehyde to one of the acid chloride so the following structure was assigned to it: $C_6H_5CH{:}CH.CHCl{-}O{-}CO$

$C_6H_5CH{:}CH.CHCl{-}O{-}CO$

Oxalyl bromide was found to react with benzaldehyde even more readily than oxalyl chloride, and the product, which was much more stable than the chlorine compound, was found to contain two molecules of the aldehyde to one of the acid bromide.

In this laboratory, the structure of the benzoyl bromide-benzaldehyde addition product was proved by Adams and Volwiler[23] to be $C_6H_5CHBr.O.COC_6H_5$, for on treatment with silver benzoate, benzylidene dibenzoate was formed. They prepared and analyzed a large number of condensation products, using substituted benzaldehydes with substituted and unsubstituted benzoyl halides and oxalyl bromide. It was found that as a rule, negatively substituted rings react more slowly than the unsubstituted or positively substituted rings. Acid chlorides were found to react more slowly than the acid

acid bromides. Oxalyl bromide reacted with aromatic aldehydes in the ratio of two molecules of the aldehyde to one of the acid bromide, yielding addition compounds that were somewhat more stable than the corresponding benzoyl bromide addition compound. Halogen substituted benzoyl chlorides seemed to have no action on benzaldehyde.

The reactions of the acid halide-aldehyde addition compounds have received but little attention, although their behavior with certain reagents has been recorded in a few instances. Thus, Descude[16] found that methylene chlor acetate reacted with ammonia or aniline to give acetamide in the one case and phenyl acetamide in the other. Potassium acetate and potassium thiocyanate simply replaced the chlorine by the acetate and thiocyanate radicles. Alcohols were found to react according to the reaction:

$$CH_2Cl\text{-}O\text{-}CO.CH_3 + 3ROH \longrightarrow CH_3COOR + H_2C\begin{matrix}OR\\OR\end{matrix} + HCl + H_2O$$

Louis Henry[17] treated methylene chlor acetate with water, and got complete decomposition into acetic acid, formaldehyde and hydrochloric acid. Sulfuric acid reacted to give a substance which Henry believed to be $CH_2(HSO_4)_2$. In the work done by Adams and Volwiler[23], the behavior of αbrom benzyl benzoate with ammonia, primary aromatic amines, water, alcohol, and silver benzoate was observed. When silver benzoate was used, the halogen was replaced by the benzoate radicle, yielding benzylidene dibenzoate. Primary aromatic amines yielded the hydrobromides of benzylidene anilines.

In the remaining cases the addition compound reacted like a mere mixture of benzoyl bromide and benzaldehyde. Thus, with dry ammonia gas in ether solution, benzamide, ammonium bromide, and benzaldehyde were obtained. Water decomposed the compound with the formation of benzoic acid, benzaldehyde, and hydrobromic acid. Alcohol reacted in a similar manner, except that ethyl benzoate rather than benzoic acid was formed.

III. THEORETICAL

Owing to the fact that the addition of acid halides to aldehydes has received such little attention, with the exception of a few isolated cases, the problem has been made the subject of considerable investigation in this laboratory, the purpose being to determine the scope of the reaction, the ease with which it takes place, and finally to study the properties of the substances formed.

The addition of acid halides to aldehydes is a general reaction in both the aromatic and alifatic series. Former investigators showed that acetaldehyde[7] and polyoxymethylene[10] would react with acid chlorides in general, forming fairly stable addition products, but little further work was accomplished in the alifatic series. Adams and Ulich[18] finally showed that the addition of alifatic acid halides to alifatic aldehydes and of aromatic acid halides to alifatic aldehydes are general reactions. The results of the present investigation on the action of aromatic acid halides on aromatic aldehydes, together with the work of Adams and Volwiler[23], demonstrate that the reaction is a general one for this series also. A large number of addition products were prepared from acid halides and aldehydes, most of which had positive or negative substituents in either one or both of the aromatic nuclei, although some were unsubstituted. As a rule, solid products were obtained from acid bromides, but in a number of cases, particularly where there were positive substituents in either ring, the substances formed were oils, and because these decomposed on distillation, even in vacuo, it was impossible to isolate the simple addition products. When treated with pyridine, these oils yielded stable addition products, a reaction which is general for the acid halide-aldehyde addition compounds. The substances formed by this treatment are crystalline, and are easily purified and analyzed. Acid chlorides showed a

greater tendency to form oils than did the acid bromides. Thus, the benzoyl chloride-benzaldehyde compound is an oil while the corresponding bromine compound is a solid, melting at 70°. Just as when oils were obtained with acid bromides, these oily substances can be isolated and analyzed as the pyridine addition products. There was also a marked tendency on the part of the acid chloride-aldehyde mixtures to fail to react completely, resulting in the formation of mushy products from which unchanged acid chloride and aldehyde can be extracted. Out of eight solid acid chloride-aldehyde addition compounds which were analyzed, four were isolated from mixtures in which the reaction did not go to completion.

Adams and Volwiler[23] were unable to isolate addition products from the action of halogen substituted benzoyl chlorides on benzaldehyde, but whether this was due to a failure to react, or whether the reaction products were oils was not determined. It was of interest to find out if aromatic aldehydes in general react in the same manner with these acid chlorides. Only one reaction of this type was tried, that of para brom benzoyl chloride and para brom benzaldehyde. The substances were found to react slowly, giving a semi-solid product, from which a stable addition compound melting at 124-125° was isolated.

But while this reaction is a general one, since practically all acid halides and aldehydes respond, the individual compounds differ greatly in the ease of formation. In the alifatic series, it has been found necessary to heat the substances[18], sometimes under pressure[7], in order to cause the reaction to take place, but in the aromatic series, it is simply necessary to mix equimolecular amounts of the acid halide and aldehyde and allow them to stand at room temperature in a tightly stoppered flask until solid. A thorough

study of the catalytic action of zinc chloride was not made, but in all of the cases where it was tried, it was found very effective. For example, benzoyl bromide and benzaldehyde react at room temperature to give a solid product in the course of a couple of days, but when a piece of anhydrous zinc chloride was added to the mixture, they reacted with the evolution of considerable heat, and formed a solid product in from three to four hours. Similarly, the time for reaction of para iod benzoyl bromide and benzaldehyde was reduced from four hours to forty-five minutes.

The ease of reaction is materially affected by different substituents in the acid halide and aldehyde nuclei. Thus, it required 100 hours for a mixture of 3-5 dinitro benzoyl bromide and ortho brom benzaldehyde to solidify, while para nitro benzoyl bromide and anisic aldehyde solidified in five minutes. Symmetrical dinitro benzoyl bromide gave a solid product with para brom benzaldehyde in two hours, and with benzaldehyde in one hour, while anisic aldehyde required but twenty minutes. Other examples of the same nature were found in the course of the present investigation. The results seem to indicate that negative substituents in either nucleus tend to retard the speed of reaction, while positive substituents cause a more rapid reaction.

Acid chlorides were found to react more slowly than the corresponding acid bromides. For example, para brom benzoyl bromide and para brom benzaldehyde reacted to give a solid product in one hour, while para brom benzoyl chloride with the same aldehyde required twenty-four hours for complete reaction. Similarly, 3-5 dinitro benzoyl bromide and benzaldehyde formed a solid product in one hour, while 3-5 dinitro benzoyl chloride and benzaldehyde required 52 hours. There is, however, a marked tendency on the part of these

addition products to form oils from which crystals are deposited very slowly, although if innoculated, crystallization would probably begin much sooner. This fact makes it impossible to get accurate data relative to the time necessary for complete reaction, and no general conclusion can be drawn relative to the effect of various substituting groups on the exact speed of reaction.

The stability of the addition products of different aromatic acid halides and aromatic aldehydes was found to vary greatly, the 3-5 dinitro benzoyl bromide-benzaldehyde compound showing but slight decomposition after being covered with water for one and one-half hours, while the 3-5 dinitro benzoyl bromide-anisic aldehyde compound was so unstable that it was impossible to purify it sufficiently for analysis. It was found to be a fairly general rule that negative substituents in either aromatic mucleus caused the formation of comparatively stable substances, while positive substituents resulted in the production of more unstable compounds, or oils which decomposed on distillation in vacuo. In the present investigation, it was found impossible to obtain in a pure condition any addition compound containing a positive substituent in either ring, although they could be isolated and purified as the pyridine addition compounds. The addition products of benzaldehyde with meta chlor benzoyl bromide, and ortho and meta iod benzoyl bromides were too unstable to analyze.

A. STRUCTURE OF THE ADDITION COMPOUNDS.

Since addition reactions with aldehydes always occur on the carbonyl group, in the addition of acid halides to aldehydes a similar reaction on the aldehyde carbonyl group would be expected. There is also a carbonyl group in the acid halide molecule, and while it is not so reactive as the one in the aldehyde, there was a question as to whether it might not also be involved. Consequently, in considering the structure of the addition compound, several possibilities presented themselves but most of them could be eliminated at once as involving very improbable reactions such as the shifting of the aldehyde hydrogen to the carbon end of the acid halide carbonyl group, or the shifting of the halogen to the oxygen of the aldehyde, or the formation of such very unstable substances as a four membered ring containing either a peroxide linkage, or two ether linkages. The two most probable structures for the addition are represented by the formulas $C_6H_5CHBr-O-COR$ and $C_6H_5-\underset{\underset{O}{|}}{C}-\overset{\overset{OH}{|}}{C}-R$ (with Cl on the second carbon)

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in the first of which the halogen adds to the carbon end of the aldehyde carbonyl group, and in the second the aldehyde hydrogen shifts to the oxygen end of the acid halide carbonyl group. The second formula seemed less probable because of the instability of compounds in which there is a hydroxyl group and a halogen on the same carbon. Then additions to the carbonyl group of acid halides are very seldom met with, while additions to the aldehyde carbonyl group are among the most common reactions of aldehydes.

The first proof of structure offered for these substances was by Schiff[4], who treated the acetaldehyde-acetyl chloride addition compound with potassium acetate and obtained ethylidene di-

acetate, thus proving the substance to be α chlor ethyl acetate, which corresponds to formula I. Later, Rubencamp[7] prepared a whole series of addition compounds from different acid chlorides and acetaldehyde, and by treating these substances with the silver salts of different acids he obtained a series of ethylidene derivatives homologous to Schiff's ethylidene diacetate. Similarly, Descude[10] prepared a number of acid chloride addition compounds with polyoxymethylene which, when treated with the potassium salts of organic acids, yielded methylene di-esters. It was therefore evident that the substances formed by the addition of acid chlorides to acetaldehyde and polyoxymethylene produced halogen esters corresponding to formula I. These results made it highly probable that the same formula represented the structure of the aromatic addition products. Adams and Volwiler[23] proved such to be the case. They chose the benzoyl bromide-benzaldehyde addition compound as representative of the whole class, and on treatment of this substance with silver benzoate, benzylidene dibenzoate was obtained.

B. REACTIONS OF ADDITION COMPOUNDS.

There are two types of reactions given by the acid halide-aldehyde addition compounds; in some cases they react like simple mixtures of aldehydes and acid halides, and in others, the reactions are characteristic of the addition compounds. A few of the reactions of phenyl brom methyl benzoate were studied by Adams and Volwiler[23]. They found that with water, the addition product behaved as though it were a simple mixture of benzoyl bromide and benzaldehyde, yielding benzoic acid, benzaldehyde, and hydrobromic acid.

$$C_6H_5CHBr.O.CO.C_6H_5 + H_2O \longrightarrow C_6H_5COOH + C_6H_5CHO + HBr$$

When treated with alcohol, a similar reaction took place, producing ethyl benzoate, benzaldehyde and hydrobromic acid.

$$C_6H_5CHBr.O.CO.C_6H_5 + C_2H_5OH \longrightarrow C_6H_5COOC_2H_5 + C_6H_5CHO + HBr$$

An ether solution of phenyl brom methyl benzoate reacted almost immediately with dry ammonia, producing benzamide, benzaldehyde and ammonium bromide.

$$C_6H_5CHBr.O.CO.C_6H_5 + 2NH_3 \longrightarrow C_6H_5CO.NH_2 + C_6H_5CHO + NH_4Br$$

When aniline was used, a reaction characteristic of the addition compound was obtained. The products formed were benzoic acid and the hydrobromide of benzylidene aniline, which were produced in practically quantitative yields. Treatment of the hydrobromide of the benzylidene aniline with alkali liberated the free base.

$$C_6H_5CHBr\text{-}O\text{-}CO\text{-}C_6H_5 + C_6H_5NH_2 \longrightarrow C_6H_5\overset{\overset{H}{|}}{\underset{Br}{C}}\text{-}\overset{\overset{H}{|}}{N}\text{-}C_6H_5 + C_6H_5COOH.$$

$$\downarrow NaOH$$

$$C_6H_5CH{:}NC_6H_5 + NaBr + H_2O$$

The fact that no trace of benzanilide could be found showed that there was no preliminary dissociation into benzoyl bromide and benzaldehyde. In the same way, the reaction with ortho toluidine formed practically quantitative yields of benzoic acid and the hydrobromide of benzylidene ortho toluidine.

The reaction with silver benzoate was, as mentioned before, characteristic of the addition compound, since the bromine was replaced by the benzoate radicle, forming benzylidene dibenzoate.

$$C_6H_5CHBr.O.CO.C_6H_5 + C_6H_5COOAg \longrightarrow C_6H_5CH(O.CO.C_6H_5)_2 + AgBr.$$

In studying the reactivity of these substances, in the present investigation, phenyl brom methyl benzoate was chosen as characteristic of the whole class of acid halide-aldehyde addition products, in the first place because the benzoyl bromide and benzaldehyde necessary for its preparation are easily obtained pure in rel-

atively large amounts, and also because those substances react readily to give an addition compound which is sufficiently stable to be handled with ease.

1. Reactions With Amines.

The reactions between phenyl brom methyl benzoate and alifatic amines were carried out in dry ether sclutions, and in every case they started within a few minutes and proceeded smoothly, giving practically quantitative yields of the products produced.

In its reaction with methylamine, phenyl brom methyl benzoate behaved as a mixture of benzoyl bromide and benzaldehyde, giving methyl benzamide, methyl amine hydrobromide, and benzylidene methyl amine.

$$C_6H_5CHBr\text{-}O\text{-}CO\text{-}C_6H_5 + 3CH_3NH_2 \longrightarrow C_6H_5\overset{\overset{O}{\|}}{C}\text{-}NHCH_3 + CH_3NH_2.HBr + C_6H_5\overset{\overset{H}{|}}{C}{:}N.CH_3$$

With diethyl amine, similar results were obtained, as diethyl benzamide, benzaldehyde and diethyl amine hydrobromide were the substances formed.

$$C_6H_5CHBr\text{-}O\text{-}CO\text{-}C_6H_5 + 2(C_2H_5)_2NH \longrightarrow C_6H_5\overset{\overset{O}{\|}}{C}\text{-}N(C_2H_5)_2 + C_6H_5CHO + (C_2H_5)_2NH.HBr$$

In this case, there was a more vigorous reaction, and enough heat was generated to make the ether boil.

The reaction with trimethyl amine was of a different type, being characteristic of the phenyl brom methyl benzoate in that an addition compound was formed.

$$C_6H_5CHBr\text{-}O\text{-}CO\text{-}C_6H_5 + (CH_3)_3N \longrightarrow C_6H_5\underset{\underset{Br\text{-}N(CH_3)_3}{|}}{CH}\text{-}O\text{-}CO\text{-}C_6H_5$$

In most cases, the reactions of phenyl brom methyl benzoate with primary aromatic amines were run without any solvent, although the same substances were obtained when the reaction took place in dry ether solution. A very vigorous reaction took place

when no solvent was used, and the materials fused together with the evolution of a great deal of heat, and becoming a hard brittle mass when cold. When an ether solution was used, the reaction began immediately, as evidenced by the precipitate which began to form, but there was no heat evolved.

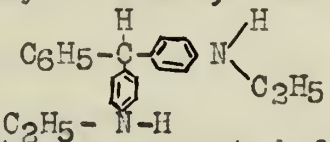
With secondary and tertiary amines, the reactions, which were carried out in dry ether solutions, did not take place so readily and the mixtures were always refluxed for varying lengths of time.

As previously mentioned, Adams and Volwiler[23] studied the reaction of phenyl brom methyl benzoate with aniline and ortho toluidine, and found that the hydrobromides of benzylidene aniline and benzylidene ortho toluidine were produced. In order to find out whether this reaction with primary aromatic amines was general, the behavior of phenyl brom methyl benzoate with ortho and para chlor aniline and with para toluidine was studied, and in every case the reaction was analogous to that of aniline.

$$C_6H_5CHBr\text{-}O\text{-}CO\text{-}C_6H_5 + ArNH_2 \longrightarrow C_6H_5\underset{Br}{\overset{H}{C}}\text{—}N\text{-}Ar + C_6H_5COOH.$$

Secondary and tertiary aromatic amines react in a different manner, producing dyes of the triphenyl methane series. With diphenyl amine both the leuco base and the dye itself were formed, an indication that dissociation into the acid bromide and aldehyde takes place, with the acid halide reacting to give the dye and the aldehyde producing the leuco base. Two precipitates were formed, the first was practically colorless, but gradually turned green on exposure to the air, while the second was a gummy, green material. These were ground up together and extracted with a large volume of ether. From the ether extract was obtained a white solid which be-

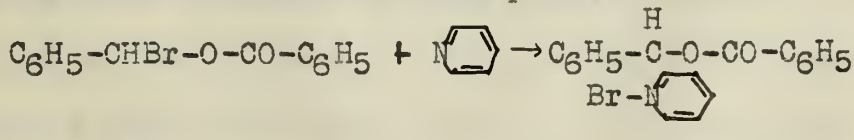
came green on being exposed to the air. Evidently, the two precipitates are the leuco base and the dye. The amount of the leuco base was small, no doubt due to oxidation during the interval of three days before the material was worked up. That diphenyl amine reacts with benzaldehyde to give the leuco base and with benzoyl chloride to give the dye was shown by Meldola[28], although the yield of the dye was small. Since only two moles of the diphenyl amine were used, the presence of free benzaldehyde in the reaction mixture would be expected if the benzoyl bromide reacted to give some of the dyestuff. That no benzaldehyde was found might have been due to its oxidation to benzoic acid before the mixture was worked up.

With mono ethyl aniline, a similar reaction took place, but only the leuco base, 
was produced. This substance separated from the ether solution of the reaction mixture as a red gummy material, and on oxidation yielded a green solution. It was first prepared and studied by Schiff[27].

Dimethyl aniline reacted slowly to produce malachite green, and the mixture was refluxed for several hours before the dye was completely precipitated. The leuco base was not isolated, although it was no doubt formed as an intermediate product.

2. Reactions With Pyridine.

The reaction with pyridine was also characteristic of the addition compound, and was analogous to the one with trimethyl amine in that an addition took place.



No solvent was used in this reaction, the phenyl brom methyl benzo-

ate was simply dissolved in a small excess of pyridine, and the mixture allowed to stand until the product had crystallized out. This addition compound was a stable substance, easily purified and analyzed. Since this pyridine addition product was so easily obtained in a pure condition, it was believed that the products from acid halide-aldehyde reactions which could not be isolated because of their instability, or because they were oils, could be shown to be the simple addition compounds by treating with pyridine and isolating the addition product. The reaction was tried out with three such substances. Equimolecular amounts of benzoyl chloride and benzaldehyde were mixed and a piece of anhydrous zinc chloride was added. A vigorous reaction took place with the evolution of a great deal of heat. When cold, the oil was poured into an excess of pyridine. The solid material thus obtained, after purification, was analyzed and found to be the pyridine addition compound, $C_6H_5CH(Cl\text{-}N\langle\bigcirc\rangle)\text{-}O\text{-}CO\text{-}C_6H_5$, indicating that the product from the reaction between the benzoyl chloride and benzaldehyde was the α chlor benzyl benzoate.

In the same way, the semi solid product obtained from the action of ortho methyl benzoyl bromide and benzaldehyde formed the pyridine addition product, $C_6H_5CH(Br\text{-}N\langle\bigcirc\rangle)\text{-}O\text{-}CO\text{-}C_6H_4(CH_3)$, showing that the aldehyde and acid halide had reacted in the normal way.

Finally, the para nitro benzoyl bromide-anisic aldehyde reaction product, which is an unstable solid, was shown by means of the pyridine addition to be the normal acid halide-aldehyde compound.

It has also been found possible to prepare these pyridine addition compounds by adding the aldehyde to the benzoyl halide-pyridine addition product. Thus, benzoyl bromide and pyridine react to form a solid substance, which on treatment with benzaldehyde yields the phenyl brom methyl benzoate-pyridine addition compound.

Benzoyl chloride was found to act in a similar manner.

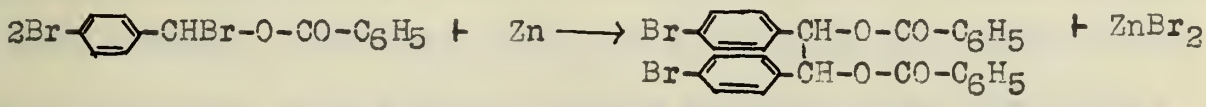
3. Reactions With Metals.

A study was made of the behavior of phenyl brom methyl benzoate with different metals, in most cases using an ether solution, although in one instance benzene was used. The only product isolated from these reactions was symmetrical diphenyl ethylene glycoll, which was obtained in largest yields (20%) when zinc dust or copper powder was used. Metallic sodium produced only a trace of this substance, while none was found when aluminum powder or magnesium shavings were used. In every case, a large amount of resinous material was formed. The reaction can be expressed as follows, using zinc as an example,

$$2C_6H_5CHBr\text{-}O\text{-}CO\text{-}C_6H_5 + Zn \longrightarrow \begin{matrix} C_6H_5\text{-}CH\text{-}O\text{-}CO\text{-}C_6H_5 \\ | \\ C_6H_5\text{-}CH\text{-}O\text{-}CO\text{-}C_6H_5 \end{matrix} + ZnBr_2$$

This same substance was prepared by Paal[29] by the action of zinc dust on a mixture of benzoyl chloride and benzaldehyde, and by Klinger and Standke[30] by the action of sodium amalgam on the same mixture.

Para brom phenyl brom methyl benzoate in dry ether was found to react with zinc dust in the same way, producing a 20% yield of the dibenzoate.



Meta nitro phenyl brom methyl benzoate was not acted upon by the zinc.

4. Reactions With Potassium Cyanide and Alkali Salts of Organic Acids.

It was found by Davis[31] that if an acid chloride was added to a mixture of potassium cyanide and an aldehyde, a substance

of the structure, R-CH(CN)-O-COR' was formed. It was suggested that the intermediate formation of the cyanhydrin took place, and this reacting with the acid halide, produced the substance obtained. In view of the results of the present investigation, it seemed probable that instead of cyanhydrin formation, an intermediate acid halide-aldehyde addition took place, and this reacted with the potassium cyanide to replace the bromine by the cyanide. With the intention of deciding this point, phenyl brom methyl benzoate was added to an aqueous solution of potassium cyanide, but although the experimental conditions were kept as nearly as possible to those used by Davis, only complete hydrolysis of the addition compound took place, yielding benzoic acid as the only solid product. It was likewise found impossible to replace the bromine by the cyanide radicle by shaking an aqueous solution of potassium cyanide and either a petrol ether or alcohol free ether solution of phenyl brom methyl benzoate together. Whenever a reaction did take place, it resulted in the formation of benzoic acid as the only solid product.

Adams and Volwiler[23] obtained benzylidene dibenzoate on treatment of phenyl brom methyl benzoate with silver benzoate, and it was of interest to find out if a concentrated aqueous solution of potassium benzoate would react in the same way. Complete hydrolysis resulted however. Similar results were obtained with concentrated aqueous solution of potassium acetate and potassium hydroxide. An absolute ether suspension of potassium hydroxide also decomposed the addition compound, with the formation of benzaldehyde and potassium benzoate.

An attempt was made to reduce the benzoyl bromide-benzaldehyde addition compound to benzyl benzoate, using aluminum amalgam and moist ether, but again complete hydrolysis took place, and only benzoic acid and benzaldehyde were produced.

IV. EXPERIMENTAL

I. FORMATION OF THE ACID BROMIDE-ALDEHYDE ADDITION COMPOUNDS.

Equimolecular amounts of the two substances were mixed without solvent in a small Erlenmeyer flask, which was then stoppered and the mixture allowed to stand until it had solidified. Many of these compounds showed a tendency to remain as oils, which thus made it necessary to rub the walls of the flask with a glass rod before the material would become solid. This tendency made it impossible to determine the exact time necessary for complete reaction. In some cases the addition compound was an oil which could not be made to solidify, and which decomposed in distillation in vacuo. In most of those cases there was no attempt made to analyze the product, but in the remaining cases the products were treated with pyridine in slight excess, and the solid pyridine addition compounds, which are easily purified by dissolving in absolute alcohol and precipitating with absolute ether, were analyzed. These addition compounds consist of one molecule of pyridine and one of the acid halide-aldehyde compound.

The same general procedure was followed in the preparation of all of the acid bromide-aldehyde addition compounds.

The acid bromides used in this research, with the exception of benzoyl bromide, were made after the method of Adams and Ulich[20], by the action of oxalyl bromide[21] on the sodium salt of the acid. Benzoyl bromide[22] was made by heating on a steam cone a mixture of phosphorous tribromide and benzoic acid. In the preparation of benzoyl bromide, it was found that much better yields could be obtained if the heating were continued for several hours and the reaction mixture were kept well stirred with an electric stirrer.

Meta Nitro Benzoyl Bromide and Benzaldehyde.

When 3.3 grams (1 mole) of meta nitro benzoyl bromide and 1.5 grams (1 mole) of benzaldehyde were mixed, without solvent, a dark red oil was obtained. Apparently it did not change on standing over night, but it solidified when scratched with a glass rod. This solid substance was pulverized, washed with absolute ether, in which it is somewhat soluble, and then crystallized from ligroin. The crystals thus obtained were pure white, and melted at 94-96°.

Analysis: weight of subs.	.1062
weight of AgBr	.0596
% Br calc. for $C_{14}H_{10}O_4NBr$,	23.81%
% Br found,	23.87%

Meta Nitro Benzoyl Bromide and Cinnamyl Aldehyde.

When 2 grams (1 mole) of meta nitro benzoyl bromide and 1.1 grams (1 mole) of cinnamyl aldehyde were mixed without solvent, they reacted immediately with the evolution of considerable heat. The mixture solidified on standing over night, but was found to be too unstable to purify sufficiently for analysis.

Para Nitro Benzoyl Bromide and Benzaldehyde.

5 grams (1 mole) of para nitro benzoyl bromide mixed with 2.3 grams (1 mole) of benzaldehyde reacted almost immediately and the resulting solution became solid within thirty minutes. The substance was pulverized, washed with hexane, then with absolute ether, after which it was recrystallized from ligroin. The pure crystals were white and had a melting point of 139-140°.

A small portion of the pure material, after standing for one minute in water, was found to be about half decomposed.

Analysis: weight of subs. .1987

weight of AgBr .1123

% Br calc. for $C_{14}H_{10}O_4NBr$ 23.81%

% Br found 24.05%

Para Nitro Benzoyl Bromide and Ortho Brom Benzaldehyde.

5 grams (1 mole) of para nitro benzoyl bromide reacted slowly with 4 grams (1 mole) of ortho brom benzaldehyde[23], going completely into solution only after standing for two hours. In fifteen hours the material was solid. This solid substance was pulverized, washed with absolute ether, and purified by dissolving in benzene and precipitating with petrol ether. The product obtained in this way melted 141-2°.

Analysis: weight of subs. .2036

weight of AgBr .1809

%Br calc. for $C_{14}H_9O_4NBr_2$ 38.55%

%Br found 37.99%

Para Nitro Benzoyl Bromide and Para Brom Benzaldehyde.

4 grams (1 mole) of para nitro benzoyl bromide were added to 3.2 grams (1 mole) of fused para brom benzaldehyde[24]. As the mixture cooled down the product solidified. This was pulverized, washed with absolute ether, crystallized from ligroin, and analyzed. M.P. 146°.

Analysis: weight of subs. .2026

weight of AgBr .1812

%Br calc. for $C_{14}H_9O_4NBr_2$ 38.55%

%Br found 38.05%

Para Nitro Benzoyl Bromide and Anisic Aldehyde.

An immediate reaction took place with the evolution of

considerable heat when equimolecular amounts of para nitro benzoyl bromide and anisic aldehyde were brought together. The mixture solidified in about five minutes. The product was very unstable, however, and on crystallization from benzene only para nitro benzoic acid was obtained.

Para Nitro Benzoyl Bromide and Cinnamyl Aldehyde.

3.8 grams (1 mole) of cinnamyl aldehyde reacted vigorously with 5 grams (1 mole) of para nitro benzoyl bromide, giving off considerable heat, and forming a greenish-black solid in about five minutes. The product was very unstable and only para nitro benzoic acid was obtained on crystallization from benzene.

3-5 Dinitro Benzoyl Bromide and Benzaldehyde.

5 grams (1 mole) of 3-5 dinitro benzoyl bromide and 1.9 grams (1 mole) of benzaldehyde reacted to give a solution almost immediately. This solution began to deposit crystals in a few minutes, and was solid within an hour. After pulverizing the material, it was washed with hexane and crystallized from ligroin. M.P. 126-127°.

A small portion of the pure substance was found to be but slightly decomposed after standing in water for one and one-half hours.

Analysis:	weight of subs.	.2096
	weight of AgBr	.1056
%Br calc. for	$C_{14}H_9O_6N_2Br$	20.99%
%Br found		21.43%

3-5 Dinitro Benzoyl Bromide and Para Brom Benzaldehyde.

When 5 grams (1 mole) of 3-5 dinitro benzoyl bromide and

3.3 grams (1 mole) of para brom benzaldehyde were mixed, an oil was obtained which solidified in two hours. This material was finely powdered, washed with hexane, and crystallized from ligroin. M.P. of the pure crystals 151-2°.

Analysis:	weight of subs.	.1953
	weight of AgBr	.1590
%Br calc. for	$C_{14}H_8O_6N_2Br_2$	34.78%
%Br found		34.64%

3-5 Dinitro Benzoyl Bromide and Ortho Brom Benzaldehyde.

5 grams (1 mole) of 3-5 dinitro benzoyl bromide reacted with 3.3 grams (1 mole) of ortho brom benzaldehyde to give a solid product in about four days. This solid material was pulverized, washed several times with hexane and absolute ether, and was crystallized from ligroin. The crystals obtained in this manner melted at 119-122°.

A portion of the pure material showed but partial decomposition after being covered with water for four hours.

Analysis:	weight of subs.	.2047
	weight of AgBr	.1690
%Br calc. for	$C_{14}H_8O_6N_2Br_2$	34.78%
%Br found		35.13%

3-5 Dinitro Benzoyl Bromide and Anisic Aldehyde.

Equimolecular amounts of the two substances reacted almost immediately, with the evolution of a large amount of heat. The mixture solidified in about twenty minutes, but the product was very unstable and decomposed completely during the process of crystallization, giving 3-5 dinitro benzoic acid.

Ortho Chlor Benzoyl Bromide and Benzaldehyde.

5 grams (1 mole) of ortho chlor benzoyl bromide and 2.4 grams (1 mole) of benzaldehyde reacted as soon as they were mixed, giving off a large amount of heat. It required seventy hours, however, for the mixture to become solid. After being finely powdered, the material was crystallized from petrol ether. M.P. 62-63°.

Analysis:	weight of subs.	.2006
	weight of mixed silver halides calc. for $C_{14}H_{10}O_2BrCl$	.2042
	weight of mixed silver halides found	.2042

Meta Chlor Benzoyl Bromide and Benzaldehyde.

Equimolecular amounts of meta chlor benzoyl bromide and benzaldehyde reacted to give an orange colored solution which began to deposit crystals in about 70 hours, although it never became solid. The product was very unstable and decomposed completely during the process of crystallization, and meta chlor benzoic acid was the only solid product isolated.

Para Chlor Benzoyl Bromide and Benzaldehyde.

When 5 grams (1 mole) of para chlor benzoyl bromide and 2.4 grams (1 mole) of benzaldehyde were mixed a yellow solution was obtained which solidified in three hours. The material was pulverized and recrystallized from ligroin. The pure material melted 110-111°.

Analysis:	weight of subs.	.1590
	weight of mixed silver halides calc. for $C_{14}H_{10}O_2BrCl$	.1619
	weight of mixed silver halides found	.1654

Ortho Brom Benzoyl Bromide and Benzaldehyde.

6.3 grams (mole) of ortho brom benzoyl bromide and 2.5 grams (1 mole) of benzaldehyde reacted to give a yellow solution, which solidified on standing over night. After crushing and washing with dry ether, the material was recrystallized from ligroin. M.P.80°

Analysis:	weight of subs.	.1955
	weight of AgBr	.1974
%Br calc. for	$C_{14}H_{10}O_3Br_2$	43.24%
%Br found		42.96%

Ortho Brom Benzoyl Bromide and Para Brom Benzaldehyde.

When 4 grams (1 mole) of ortho brom benzoyl bromide and 2.8 grams (1 mole) of para brom benzaldehyde were mixed, a great deal of heat was evolved by the reaction. In about twenty minutes the dark red solution deposited crystals and the mixture got very warm. In forty minutes the material was solid. The substance was pulverized, washed with dry ether, and recrystallized from ligroin. M.P. 102-3°.

Analysis:	weight of substance	.1981
	weight of AgBr	.2506
%Br calc. for	$C_{14}H_9O_2Br_3$	53.45%
%Br found		53.82%

Para Brom Benzoyl Bromide and Benzaldehyde.

No reaction was apparent when 5 grams (1 mole) of para brom benzoyl bromide were mixed with 2 grams (1 mole) of benzaldehyde, but the material solidified after standing over night. The substance was worked up in the usual way. Melting point of the pure material 119-121°.

Analysis: weight of subs.	.2013
weight of AgBr	.2028
% Br calc. for $C_{14}H_{10}O_2Br_2$	43.34%
% Br found	42.87%

Para Brom Benzoyl Bromide and Ortho Brom Benzaldehyde.

5 grams (1 mole) of para brom benzoyl bromide and 3.5 grams (1 mole) of ortho brom benzaldehyde reacted to give a solution which solidified in five hours. This solid material was finely powdered, washed with dry ether, and recrystallized from ligroin. The crystals obtained in this way were white and melted 154-6°.

Analysis: weight of subs.	.1965
weight of AgBr	.2470
%Br calc. for $C_{14}H_9O_2Br_3$	53.45%
%Br found	53.48%

Para Brom Benzoyl Bromide and Para Brom Benzaldehyde.

5 grams (1 mole) of para brom benzoyl bromide and 3.5 grams (1 mole) of para brom benzaldehyde reacted in half an hour, with the absorption of considerable heat. Within an hour, the material was solid. It was washed with absolute ether and recrystallized from ligroin in the usual way. M.P. 120-121°.

Analysis: weight of subs.	.2000
weight of AgBr	.2511
% Br calc. for $C_{14}H_9O_2Br_3$	53.45%
% Br found	53.42%

Para Brom Benzoyl Bromide and Anisic Aldehyde.

Equimolecular amounts of the two substances were mixed, and they solidified immediately with the evolution of considerable

heat. This material was very unstable and decomposed completely before it could be purified sufficiently for analysis.

Para Iod Benzoyl Bromide and Benzaldehyde.

When 5 grams 1 mole) of para iod benzoyl bromide and 1.7 grams (1 mole) of benzaldehyde were mixed, solution took place in a few minutes with the absorption of considerable heat. This solution solidified in four hours. When the experiment was repeated and a small piece of zinc chloride (fused) was added to the mixture, solidification took place in forty-five minutes.

The product was worked up in the usual way. The pure substance gave a melting point of 123.5-124°.

Analysis: weight of subs. .2032

weight of mixed silver halides calc. for $C_{14}H_{10}O_2BrI$ .2060

weight of mixed silver halides found .2068

Ortho Iod Benzoyl Bromide and Benzaldehyde.

2 grams (1 mole) of ortho iod benzoyl bromide added to .7 gram (1 mole) of benzaldehyde reacted vigorously with the evolution of a great deal of heat. Crystallization began within ten minutes but the solid product was very unstable and decomposed in the process of purification.

Meta Iod Benzoyl Bromide and Benzaldehyde.

A reaction took place immediately when 2 grams (1 mole) of meta iod benzoyl bromide were mixed with .8 grams (1 mole) of benzaldehyde. Crystals first appeared within 2½ hours, and after standing over night a soft, semi-solid product was obtained. The material was very unstable and decomposed completely during the

process of purification.

Para Methoxy Benzoyl Bromide and Benzaldehyde.

A reaction began at once when 4.5 grams (1 mole) of para methoxy benzoyl bromide were added to 2.2 grams (1 mole) of benzaldehyde, and a considerable amount of heat was evolved. Crystals first appeared in four minutes but the substance never became completely solid. The product was very unstable and decomposed in the process of purification giving anisic acid as the only solid product.

Ortho Methyl Benzoyl Bromide and Benzaldehyde.

5 grams (1 mole) of ortho methyl benzoyl bromide were treated with 2.6 grams (1 mole) of benzaldehyde. The orange colored solution thus obtained solidified in seven hours. When the experiment was repeated, a small piece of zinc chloride was added to the mixture, and a solid product was obtained in one hour. The material was very unstable and decomposed before it could be purified sufficiently for analysis.

Meta Methyl Benzoyl Bromide and Benzaldehyde.

When equimolecular amounts of the two substances were mixed, a yellow solution was obtained, but there was no temperature change. The product, which took fifty-seven hours to solidify, was so unstable that no analysis could be made.

Para Methyl Benzoyl Bromide and Benzaldehyde.

When molecular amounts of the two substances were mixed, no reaction was apparent, and although the solution began to deposit crystals in two days, it never completely solidified, and the only material isolated from the mixture was para methyl benzoic acid.

II. FORMATION OF ACID CHLORIDE-ALDEHYDE ADDITION COMPOUNDS.

In preparing these compounds the same general procedure was followed which was used in the formation of the acid bromide-aldehyde addition compounds. The method of Adams and Ulich[20] was used in the preparation of the acid chlorides, with the exception of benzoyl chloride, which was made in the usual way from benzoic acid and PCl_5.

Benzoyl Chloride and Para Brom Benzaldehyde.

5 grams (1 mole) of benzoyl chloride reacted with 6.5 grams (1 mole) of para brom benzaldehyde to give a solution which crystallized to a semi-solid material. It never became completely solid although it stood for fifteen days. The material after recrystallization from ligroin melted 109-110°. A small portion of the pure substance showed no decomposition when shaken for a minute with water.

Analysis:	weight of subs.	.2020
	weight of mixed silver halides calc. for $C_{14}H_{10}O_2BrCl$	.2057
	weight of mixed silver halides, found	.2071

Benzoyl Chloride and Benzaldehyde.

50 grams (1 mole) of benzoyl chloride were treated with 37.5 grams (1 mole) of benzaldehyde, and a small piece of zinc chloride was added. These substances reacted to give a red solution with the evolution of a great deal of heat. There was no further change on standing over night. The oil was fractionated in vacuo as follows:

1st fraction-	boiling 77-81°	at 15 mm.
2nd fraction-	" 84-86°	at 15 mm.
3rd fraction-	" 205-208°	at 15 mm.

The first two fractions were redistilled under ordinary pressure and proved to be benzaldehyde and benzoyl chloride. The third fraction solidified in three days and was found to have a melting point of 42°. A mixed melting point with benzoic anhydride showed it to be that substance.

weight of recovered benzoyl chloride	30 grams.
weight of recovered benzaldehyde	31 grams.
weight of benzoic anhydride	10 grams.

Benzoyl Chloride and Meta Nitro Benzaldehyde.

5 grams (1 mole) of benzoyl chloride mixed with 5.3 grams (1 mole) of meta nitro benzaldehyde reacted to give a solution which required twenty days for complete solidification. This solid material, after being pulverized, was washed several times with petrol ether and recrystallized from ligroin. The pure crystals had a melting point 109-110°. A small portion of the pure substance was found to be but slightly decomposed after standing a couple of minutes in water. Very slight decomposition was noted after standing for four days in the air of the laboratory.

Analysis:	weight of subs.	.1226
	weight of AgCl	.0628
%Cl calc. for $C_{14}H_{10}O_4NCl$		12.18%
%Cl found		12.64%

3-5 Dinitro Benzoyl Chloride and Benzaldehyde.

5 grams (1 mole) of 3-5 dinitro benzoyl chloride added to 2.3 grams (1 mole) of benzaldehyde went into solution in three hours, but required 52 hours for complete solidification. The solid material was pulverized, washed with dry ether, and recrystallized from ethyl acetate. M.P. 135-136°.

Analysis:	weight of subs.	.1993
	weight of AgCl	.0872
%Cl calc. for	$C_{14}H_9O_6N_2Cl$	10.55%
%Cl found		10.82%

3-5 Dinitro Benzoyl Chloride and Para Brom Benzaldehyde.

It took three hours for 5 grams (1 mole) of 3-5 dinitro benzoyl chloride mixed with 4 grams (1 mole) of para brom benzaldehyde to liquify. This mixture never completely solidified although it was allowed to stand for eight days. When washed with petrol ether and absolute ether, two grams of the para brom benzaldehyde were recovered. The rest of the material was recrystallized from ligroin, and when pure had a melting point of 145-146°.

A portion of the pure substance showed no decomposition after being shaken for a minute with water.

Analysis:	weight of subs.	.2000
	weight of mixed silver halides calc. for $C_{14}H_8O_6N_2BrCl$	.1595
	weight of mixed silver halides found	.1570

Para Brom Benzoyl Chloride and Para Brom Benzaldehyde.

5 grams (1 mole) of para brom benzoyl chloride treated with 4.2 grams of para brom benzaldehyde, gave a solution which became semi-solid in the course of twenty-four hours, but it never completely solidified. The material was washed several times with petrol ether and absolute ether, and was recrystallized from ligroin. The pure crystals had a melting point of 134-135°.

Analysis:	weight of subs.	.2032
	weight of mixed silver halides calc. for $C_{14}H_9O_2Br_2Cl$	.2609
	weight of mixed silver halides found	.2578

Cinnamyl Chloride and Benzaldehyde.

When 10 grams (1 mole) of benzaldehyde were mixed with 15.6 grams (1 mole) of cinnamyl chloride, no apparent change took place, but after standing three days a yellow solid was obtained. Pure crystals melting at 80° were obtained by recrystallization from ligroin.

Analysis:	weight of subs.	.1968
	weight of AgCl	.1048
% Cl calc. for $C_{16}H_{13}O_2Cl$		13.02%
% Cl found		13.16%

Cinnamyl Chloride and Para Brom Benzaldehyde.

A mixture of 4.5 grams (1 mole) of cinnamyl chloride and 5 grams (1 mole) of para brom benzaldehyde gave a yellow solution which completely solidified in three hours. This material was pulverized, washed with absolute ether and recrystallized from ligroin. M.P. 92-93°.

Analysis:	weight of subs.	.2043
	weight of mixed silver halides calc. for $C_{16}H_{12}O_2BrCl$	.1925
	weight of mixed silver halides found	.1926

Cinnamyl Chlcride and Anisic Aldehyde.

Equimolecular amounts of these two substances reacted to give a solution which never solidified, and no analysis was made.

Cinnamyl Chloride and Piperonal.

Equimolecular amounts of Cinnamyl Chloride and piperonal were mixed and the resulting oil was allowed to stand in a tightly

stoppered Erlenmeyer flask. In 2½ months the material was nearly solid, but the product was unstable and on recrystallization from ligroin, cinnamic acid was the only solid obtained.

Cinnamyl Chloride and Vanillin.

5 grams (1 mole) of cinnamyl chloride added to 4.5 grams (1 mole) of vanillin gave a solution which solidified within twenty-four hours. The product was very unstable and decomposed completely in the process of crystallization.

Cinnamyl Chloride and Methyl Vanillin.

When 5 grams (1 mole) of cinnamyl chloride was treated with 5 grams (1 mole) of methyl vanillin[25], a red solution was obtained which solidified to a gummy mass within three hours, but the product decomposed before it could be purified sufficiently for analysis.

Trichlor Acetyl Chloride and Benzaldehyde.

There was no evidence of any reaction when equimolecular amounts of the two substances were mixed. The material was allowed to stand for two weeks when it was distilled in vacuo, but only benzaldehyde and trichlor acetyl chloride were obtained.

Trichlor Acetyl Chloride and Piperonal.

Equimolecular amounts of these substances when mixed reacted immediately with the evolution of heat, but when distilled in vacuo (8 mm.) only the original substances were obtained.

III. FORMATION OF PHENYL HALOGEN METHYL BENZOATE-PYRIDINE ADDITION COMPOUNDS.

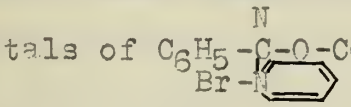
Phenyl Brom Methyl Benzoate and Pyridine.

33 grams of phenyl brom methyl benzoate were added in small portions to 150 cc. of pyridine. The material went into solution slowly but except for a very slight warming of the mixture there was no evidence of a reaction. On standing, however, crystals began to deposit and soon a very heavy precipitate had formed. The solid material was filtered off and found to be very soluble in water. The water solution, which had a neutral reaction, gave an immediate precipitate of silver bromide on the addition of silver nitrate. The material was purified by dissolving in absolute alcohol and precipitating with absolute ether. M.P. 180° with decomposition. Analysis showed it to be the addition compound of phenyl brom methyl benzoate and pyridine, $C_6H_5-\overset{H}{C}-O-CO-C_6H_5$ with Br–N (pyridine ring).

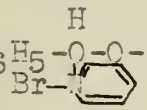
		I	II
Analysis:	weight of subs.	.5954	.5934
	No. cc. $AgNO_3$	17.14	17.14
	N.F. of $AgNO_3$ solution	.0934	.0934
	% Br calc. for $C_{19}H_{15}O_2NBr$	21.62	21.62
	% Br found	21.50	21.58

Benzoyl Bromide-Pyridine Addition Compound and Benzaldehyde.

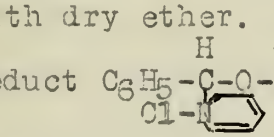
11.7 grams (1 mole) of benzoyl bromide were added to 8 grams (1½ moles) of pyridine. The reaction started at once with the liberation of a considerable amount of heat. The temperature was kept down by means of an ice bath. The solid material which resulted from the reaction, was crushed up and 6.7 grams (1 mole) of benzaldehyde were added and the mixture was stirred with a glass

rod. Considerable heat was evolved, and as the mixture cooled it set to a sticky mass, which soon became hard. This product was pulverized, washed several times with absolute ether, and purified by dissolving in absolute alcohol and precipitating with absolute ether. When the ether was first added a dark red oil separated. The clear solution was decanted from the oil and when cooled deposited white crystals of  , M.P. 179-180°.

The red oil which separated before crystallization began, solidified and when dissolved in absolute alcohol and treated with absolute ether, crystals of the addition compound separated.

Weight of  12 grams.

Benzoyl Chloride-Pyridine Addition Compound and Benzaldehyde.

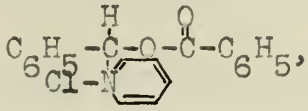
A mixture of 10 grams of benzoyl chloride and 5.6 grams of pyridine were allowed to stand over night. Only a few crystals had separated by that time. When 7.5 grams of benzaldehyde were added a reaction took place at once with the liberation of a considerable amount of heat. The mixture solidified in about ten minutes and was purified by dissolving in absolute alcohol and precipitating with dry ether. Analysis showed the compound to be the addition product  . M.P. 192° with decomposition.

		I	II
Analysis:	weight of subs.	.6210	.5910
	No. cc. $AgNO_3$	18.67	17.81
	N.F. $AgNO_3$	.1022	.1022
	%Cl calc. for $C_{19}H_{16}O_2NCl$,	10.90%	10.90%
	%Cl found	10.90%	10.93%

Benzoyl Chloride-Benzaldehyde Addition Compound and Pyridine.

The benzoyl chloride-benzaldehyde addition compound was

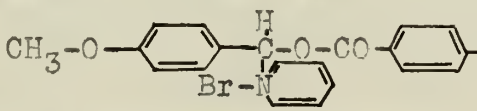
prepared by mixing 10 grams (1 mole) of benzoyl chloride and 7.5 grams (1 mole) of benzaldehyde. These substances reacted with the evolution of a considerable amount of heat, giving a red oil. This oil, when cold, was poured into 25 grams of pyridine. The mixture began to warm up, but the temperature was kept down by means of an ice bath. In about five minutes crystals began to separate, and in half an hour the mixture was solid. The solid material was filtered off and purified by dissolving in absolute alcohol and precipitating with dry ether. The product proved to be

 , M.P. 193° with decomposition.

Yield, 17 grams.

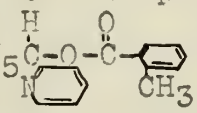
Para Nitro Benzoyl Bromide-Para Methoxy Benzaldehyde Addition Compound and Pyridine.

7 grams (1 mole) of para nitro benzoyl bromide reacted at once with 4.1 grams (1 mole) of para methoxy benzaldehyde, with the liberation of considerable heat. Crystals began to separate at once, and within two minutes a greenish yellow solid was obtained. This substance was pulverized and added in small amounts to 25 grams of pyridine. Complete solution took place. Within a few minutes crystals of the pyridine addition compound separated. The solid material was filtered off, dissolved in absolute alcohol and precipitated with dry ether. After drying in vacuo over sulfuric acid, the product was analyzed. M.P. of the compound

 , 126-128°.

Analysis:	weight of subs.	.6097
	No. cc. $AgNO_3$	13.55
	N.F.	.1023
	%Br calc. for $C_{20}H_{17}O_5N_2Br$	17.97%
	%Br found	18.17%

Ortho Methyl Benzoyl Bromide-Benzaldehyde Addition Compound and Pyridine.

There was no evidence of reaction when 5 grams (1 mole) of ortho methyl benzoyl bromide were added to 2.6 grams (1 mole) of benzaldehyde, but after standing over night, a semi solid product was obtained. This was added to one mole of pyridine and the mixture stirred with a glass rod till it solidified. This solid substance was pulverized, dissolved in absolute alcohol and precipitated with dry ether. The addition compound,  obtained in this way melted at 206° with decomposition.

		I	II
Analysis:	weight of subs.	.6630	.7751
	No. cc. $AgNO_3$	17.08	19.91
	N.F. $AgNO_3$	.1022	.1022
	%Br calc. for $C_{20}H_{18}O_3NBr$	20.83%	20.83%
	%Br found	21.06%	21.00%

IV. REACTIONS OF PHENYL BROM METHYL BENZOATE WITH AMINES.

As a rule the reactions between phenyl brom methyl benzoate and amines were carried out in dry ether solution. An exception to this procedure is found in the reactions with primary aromatic amines, most of which were carried out without a solvent, in order to make the experimental conditions the same as those under which similar reactions were carried out in previous work in this laboratory[33]. In one case the reaction with a primary aromatic amine was repeated, using dry ether as a solvent, but the products of the reaction were the same as when no solvent was used.

It was found that when phenyl brom methyl benzoate was mixed with the amines, reaction took place almost immediately, sometimes with the evolution of considerable heat, particularly in the

cases where no solvent was used. As might be expected, primary and secondary alifatic amines yielded with phenyl brom methyl benzoate, substituted benzamides, with benzaldehyde and the amine salt as the other products. From the reaction with a tertiary alifatic amine, an addition compound was obtained. The hydrobromides of substituted benzylidine anilines were produced by the action with primary aromatic amines. Secondary and tertiary aromatic amines produced dyes of the triphenyl methane type.

The phenyl brom methyl benzoate used in all the reactions studied, was freshly prepared by mixing equimolecular amounts of benzoyl bromide and benzaldehyde. A small piece of zinc chloride was added to catalyze the reaction. Usually solidification took place within three hours, after which the material was pulverized and crystallized from petrol ether (B.P. 60-70°). One crystallization always gave a pure white compound, melting 69-70°, so that further purification was unnecessary.

Phenyl Brom Methyl Benzoate and Methyl Amine.

35 grams (something over 3 moles) of methyl amine hydrochloride were dissolved in 50 cc. of water and the solution was slowly dropped into a gently boiling solution of NaOH (30 grams of NaOH in 270 cc. water). The methyl amine thus obtained was passed through two large drying towers filled with soda lime and into a solution of 45 grams of phenyl brom methyl benzoate in 400 cc. of absolute ether. A white precipitate began to form in about five minutes, increasing in amount until it was quite heavy by the time all of the amine had been added. The flask was tightly stoppered and after standing over night, the white solid was filtered off and washed with absolute ether. The white solid was analyzed and found to be methyl amine hydrobromide. The ether solution was

evaporated in vacuo and the oil thus obtained was fractionated under reduced pressure. The first fraction boiled up to 180° at 70 mm., and the second fraction up to 230° at 70 mm. This higher boiling fraction solidified and was found to be $C_6H_5-\overset{O}{\overset{\|}{C}}-N\begin{matrix}H\\ \diagdown\\ \diagup\\ CH_3\end{matrix}$, M.P.78-9°. The lower boiling fraction was distilled under ordinary pressure and proved to be benzylidene methyl amine, boiling point 180-181°.

Analysis of the methyl amine hydrobromide:

weight of subs.	.1997
No. cc. of $AgNO_3$	17.49
N.F. of $AgNO_3$	.1022
%Br calc. for CH_6NBr	71.42%
%Br found	71.60%
weight of $CH_3-NH_2.HBr$	15 grams
weight of $C_6H_5-\overset{H}{\overset{\|}{C}}:N.CH_3$	16 grams
weight of $C_6H_5\overset{O}{\overset{\|}{C}}-N\begin{matrix}H\\ \diagdown\\ \diagup\\ CH_3\end{matrix}$	16 grams

Phenyl Brom Methyl Benzoate and Diethyl Amine.

A solution of 40 grams of phenyl brom methyl benzoate in absolute ether was added slowly to an absolute ether solution of 30 grams (3 moles) of diethyl amine, and almost immediately a white precipitate of diethyl amine hydrobromide began to form. Enough heat was generated to cause the ether to boil. After standing over night the solution was filtered and the ether evaporated. The oil thus obtained was distilled in vacuo and the following fractions taken:

Fraction I C.P. 89° at 35 mm.

Fraction II Boiling 160-175° at 35 mm.

The two fractions were redistilled under ordinary pressure and were found to be benzaldehyde, boiling at 179-182°, and diethyl benzamide, boiling at 278-282°.

weight of C_6H_5CHO 10 grams

weight of $C_6H_5\overset{O}{\overset{\|}{C}}-N(C_2H_5)_2$ 16 grams

weight of $(C_2H_5)_2NH.HBr$ 21 grams

Phenyl Brom Methyl Benzoate and Trimethyl Amine.

The trimethyl amine was obtained by dropping a concentrated water solution of 100 grams of trimethyl amine hydrochloride into a hot 10% solution of sodium hydroxide. It was passed through two drying towers filled with soda lime and into a solution of 39 grams of phenyl brom methyl benzoate in 500 cc. of absolute ether. Almost immediately a white precipitate began to form and by the time the three moles of trimethyl amine had been passed into the reaction mixture the whole solution had become a thick mush. There was a slight rise in temperature. The white solid (A) was filtered off and the ether was evaporated to dryness. There was no residue. The white solid was completely soluble in water, and this solution when treated with sodium hydroxide gave off trimethyl amine. The odor of benzaldehyde could also be detected. Acidification of the sodium hydroxide solution precipitated benzoic acid. The material (A) was recrystallized from alcohol, and had a melting point of 136-137°. After drying for several weeks in vacuo over sulfuric acid, the substance was analyzed and found to be the addition compound

$$C_6H_5-\overset{H}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-O-CO-C_6H_5$$
$$\qquad\qquad\quad N(CH_3)_3$$

Analysis:

	I
weight of subs.	.2042
weight of AgBr	.1080
%Br calc. for $C_{17}H_{20}O_2NBr$	22.85%
%Br found	22.50%

II

weight of subs.	.2632
weight of AgBr	.1400
%Br calc. for $C_{17}H_{20}O_2NBr$	23.85%
%Br found	23.63%

Phenyl Brom Methyl Benzoate and Ortho Chlor Aniline.

When 10 grams (1 mole) of phenyl brom methyl benzoate and 4.3 grams (1 mole) of ortho chlor aniline were mixed without solvent, they reacted almost immediately, with the evolution of a great deal of heat. The mixture was stirred with a glass rod until it solidified, about five minutes. The yellow solid thus obtained was pulverized and washed three times with absolute ether. The ether washings yielded on evaporation 4 grams of benzoic acid (M.P. 121-122°). A portion of the yellow solid (A) remaining from the ether extraction was treated with water and found to decompose instantly into benzaldehyde and ortho chlor aniline hydrobromide. The dry solid (A) was placed in a beaker and 50 cc. of 20% sodium hydroxide were added. The ether extract of this mixture was dried over $CaCl_2$ and the ether evaporated, and the oil remaining was rubbed with a glass rod till it solidified. Its melting point was found to be 54°. A mixed melting point with some benzylidene ortho chlor aniline (prepared from benzaldehyde and ortho chlor aniline) was taken and found to be 54°. The yellow solid (A) was analyzed for bromine by the Volhard method and proved to be the hydrobromide of benzylidene ortho chlor aniline.

Analysis:	weight of subs.	.5429
	No. cc. $AgNO_3$	17.84
	N.F. of $AgNO_3$	.1022

%Br calc. for $C_{13}H_{11}NBrCl$ 26.98%

%Br found 26.86%

weight of C_6H_5COOH 4 grams

weight of $C_6H_5C(H):N-C_6H_4-Cl$ 4 grams

Phenyl Brom Methyl Benzoate and Para Chlor Aniline.

An immediate reaction took place when an absolute ether solution of 51 grams (1 mole) of phenyl brom methyl benzoate was added to an absolute ether solution of 23 grams (1 mole) of para chlor aniline. A white precipitate formed, but there was no change of temperature. After standing over night, the precipitate had become yellow in color. This material (A) was filtered off and washed with absolute ether and the combined ether solutions evaporated to dryness. Benzoic acid was the only product obtained. The yellow solid (A) was placed in a beaker and an excess of 10% sodium hydroxide was added. The ether extract of this mixture yielded on evaporation benzylidene para chlor aniline, M.P. 61-62°. This compound was prepared by Hantzsch and Schwab[26] from benzaldehyde and para chlor aniline, and was reported by them as melting at 62°.

weight of $C_6H_5-C(H)(Br)-N(H)-C_6H_4-Cl$ 46 grams

weight of C_6H_5COOH 22 grams

Phenyl Brom Methyl Benzoate and Para Chlor Aniline.

On mixing 10 grams (1 mole) of phenyl brom methyl benzoate and 4.3 grams (1 mole) of para chlor aniline, without solvent, a reaction took place at once with the evolution of a great deal of heat. The material did not liquify, but it became quite soft and sticky, and soon hardened into a yellow solid. This material was pulverized and treated with 30 cc. of 20% sodium hydroxide solution. The ether

extract of this mixture was dried over calcium chloride and the ether evaporated, and the benzylidene para chlor aniline crystallized from alcohol. M.P. 62°. The sodium hydroxide solution on acidification yielded benzoic acid.

weight of C_6H_5COOH 4 grams

weight of $C_6H_5\overset{H}{C}{:}N-C_6H_4-Cl$ 6 grams

Phenyl Brom Methyl Benzoate and Para Toluidine.

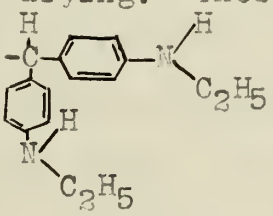
A vigorous reaction took place immediately when 10 grams (1 mole) of phenyl brom methyl benzoate was mixed with 3.7 grams (1 mole) of para toluidine. A great deal of heat was liberated and the material liquified, but soon hardened to a yellow solid. This product was pulverized and washed several times with dry ether. On evaporation of the ether, benzoic acid was obtained. The yellow solid remaining after the ether extraction was analyzed and found to be the hydrobromide of benzylidene para toluidine.

Analysis:	weight of subs.	.5949
	No. cc. $AgNO_3$	21.26
	N.F. of $AgNO_3$ sol.	.1022
	%Br calc. for $C_{14}H_{14}NBr$	28.98%
	%Br found	29.21%

Phenyl Brom Methyl Benzoate and Mono Ethyl Aniline.

When an absolute ether solution of 40.5 grams (1 mole) of phenyl brom methyl benzoate was mixed with an absolute ether solution of 33.6 grams (2 moles) of mono ethyl aniline, a bright red solution was obtained almost immediately, followed by the separation of a dark red oil, leaving a yellowish-orange colored solution. Enough heat was generated to make the ether boil. After refluxing the material for eight hours, the ether was decanted from the dark

red gummy mass (A) in the bottom of the flask. The ether was extracted successively with Na_2CO_3 solution and dilute HCl which yielded respectively 11 grams of benzoic acid and 8.5 grams of mono ethyl aniline. On evaporation of the ether .5 gram of benzaldehyde was obtained.

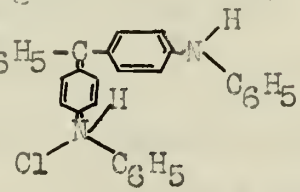
An attempt was made to reduce some of (A) with stannous chloride but there was no reaction. When oxidized with PbO_2 and HCl a green solution was obtained. An alcohol solution of (A) was red in direct light and green in reflected light. With $HgCl_2$, it gave a white precipitate which turned blue on drying. These properties correspond to those of the compound  , which is described by Schiff[37].

weight of C_6H_5COOH	11 grams
weight of recovered $C_6H_5NH.C_2H_5$	8.5 grams
weight of gummy material	48 grams

Phenyl Brom Methyl Benzoate and Diphenyl Amine.

An absolute ether solution of 57.2 grams (2 moles) of diphenyl amine was added to an absolute ether solution of 49.3 grams (1 mole) of phenyl brom methyl benzoate and the mixture was shaken vigorously. In about a minute a colorless precipitate began to form, and the solution became dark red in color, but there was no apparent temperature change. On standing for one and one-half hours the solution began to turn green and a gummy deposit formed. After standing for three days the solution was filtered and the ether was extracted with sodium carbonate solution. This alkaline extract yielded 13 grams of benzoic acid. No benzaldehyde could be found in the ether solution.

The residue left after filtering appeared to be of two kinds, a dark green, gummy mass, and a very light green, hard brittle substance, this latter being the material which precipitated first. The whole mass was ground up and extracted with a fairly large volume of ether. Alcohol was added to the ether solution and a white, gummy substance precipitated. This material turned green on exposure to air.

The residue remaining from the ether extraction was dissolved in a mixture of benzene, alcohol, and sodium hydroxide solution, giving a reddish-brown solution. On adding water, the benzene solution separated. This was washed twice with water and dried, and dry HCl gas was passed in till the solution was saturated. The hydrochloride salt precipitated as a green mass. This material was filtered, and, when dry, it was dissolved in boiling alcohol acidified with HCl. After filtering the hot solution, it was diluted with one-fourth its bulk of dilute HCl, and on cooling the hydrochloride was deposited in granular form. This behavior corresponds to that of the compound  , described by Meldola[28].

In this same reference the preparation of this dye from benzoyl chloride and diphenyl amine, and from benzaldehyde and diphenyl amine is described. The former method gives rather poor yields of the dye itself, while the latter method gives much better yields of the leuco base. Since the reaction between the phenyl brom methyl benzoate and the diphenyl amine yielded both the leuco base and the dye itself, it is evident that the phenyl brom methyl benzoate acted like a mixture of benzoyl bromide and benzaldehyde, and in order to get a maximum yield of the dye-stuff, four moles instead of two moles

of the amine should have been used. Failure to find benzaldehyde in the original ether solution might have been due to its oxidation to benzoic acid during the three days that the reaction mixture stood before being worked up. In the reaction as run, the amount of dye exceeded the amount of leuco base, due no doubt to the oxidation of the leuco base during the three days standing before the reaction mixture was worked up.

weight of C_6H_5COOH 13 grams

Phenyl Brom Methyl Benzoate and Dimethyl Aniline.

When an absolute ether solution of 39 grams (1 mole) of phenyl brom methyl benzoate was added to an absolute ether solution of 49 grams (3 moles) of dimethyl aniline, a cloudiness appeared almost immediately, but there was no other evidence of a reaction. The mixture was refluxed for four hours, by which time the solution had become slightly green in color and a small amount of a thick, viscous mass, (A), greenish brown in color, had separated. The ether solution was decanted and extracted with dilute sodium carbonate solution, then with dilute hydrochloric acid. These extracts yielded respectively 4 grams of benzoic acid and 32.5 grams of dimethyl aniline. The ether solution was dried, and the ether evaporated, and the resulting oil distilled in vacuo. At first the material was colorless, but towards the end of the distillation it suddenly became intensely green in color (B). At this point the distillation was stopped. The distillate consisted of 3.3 grams of benzaldehyde, which, together with the benzoic acid indicated above, came from the decomposition of unchanged phenyl brom methyl benzoate by the sodium carbonate solution.

The green residue (B) left in the distilling flask after

the removal of the benzaldehyde was dissolved in alcohol and the solution concentrated. In this way, a mass of green crystals was obtained.

The greenish brown viscous mass (A) left in the original reaction flask could not be made to crystallize from alcohol, so it was dissolved in water and treated with zinc and hydrochloric acid. This mixture was extracted with ether and the leuco base of malachite green was obtained. M.P. from alcohol 92-93°.

weight of benzoic acid	4 grams
weight of benzaldehyde	3.3 grams
weight of dimethyl aniline recovered	32.5 grams
weight of malachite green	3.5 grams

Phenyl Brom Methyl Benzoate and Dimethyl Aniline.

An absolute ether solution of 46.5 grams (2 moles) of dimethyl aniline was added to an absolute ether solution of 55.5 grams (1 mole) of phenyl brom methyl benzoate and the solution refluxed for nine hours. A considerable amount of a green viscous mass had separated by that time, and the solution had become very green in color. After evaporating the ether, the material was steam distilled in order to remove any unchanged dimethyl aniline as well as benzoic acid and benzaldehyde from the decomposition of any unchanged phenyl brom methyl benzoate. The distillate was extracted with ether, and the ether solution was washed first with sodium carbonate solution, then with dilute hydrochloric acid, and finally was dried over $CaCl_2$ and distilled. These procedures yielded respectively 4.2 grams of benzoic acid, 11.2 grams of dimethyl aniline, and 1.5 grams of benzaldehyde.

Treatment of the Residue from the Steam Distillation:-

As much water as possible was distilled off and an attempt

was made to recrystallize the green mass that remained. The attempt was unsuccessful. The material, weighing 55 grams, was reduced with zinc and hydrochloric acid and the leuco base of malachite green was obtained.

weight of recovered $C_6H_5N(CH_3)_2$	11.2 grams
weight of C_6H_5COOH	4.2 grams
weight of C_6H_5CHO	1.5 grams

V. REACTIONS OF PHENYL BROM METHYL BENZOATE AND SUBSTITUTED BENZOATE WITH METALS AND ALUMINUM AMALGAM.

Phenyl Brom Methyl Benzoate and Zinc.

3.9 grams ($\frac{1}{2}$ mole) of zinc dust were divided into two portions and these added separately to a solution of 25 grams of phenyl brom methyl benzoate in 300 cc. of absolute ether. The solution slowly turned dark red in color. After refluxing the mixture for five hours, the zinc was filtered off and the ether evaporated. In this manner, there was obtained a dark red oil which solidified on standing. This material was washed with absolute ether and recrystallized from benzene. The pure white crystals thus obtained melted at 246-247°. The melting point recorded in the literature for the compound, $C_6H_5-\underset{H}{\overset{H}{C}}-O-CO-C_6H_5$, is 247°. The water extract of
$C_6H_5-\underset{H}{\overset{|}{C}}-O-CO-C_6H_5$

the zinc gave qualitative tests for zinc and bromine.

Phenyl Brom Methyl Benzoate and Zinc.

35 grams of zinc dust were divided into three portions and these added separately to a solution of 28 grams of phenyl brom methyl benzoate in 300 cc. of ether, the mixture being kept well shaken during the process. After the first addition there was no

apparent change for two or three minutes, then the mixture began to warm up rapidly till the ether began to boil vigorously. As soon as this reaction had ceased the other two additions of zinc were made, but there was no apparent reaction. The zinc dust was filtered off at once and extracted three times with boiling ether. These ether extractions were added to the original ether solution and the whole concentrated to a volume of 100 cc. The white flocculent material which separated was filtered off and recrystallized from benzene. M.P. of the dibenzoate 245-246°.

The filtrate from the dibenzoate was concentrated still further, and a very thick, viscous mass was obtained. This on treatment with sodium hydroxide solution yielded benzoic acid, M.P. 121-122°. The resinous matter left from this treatment could not be made to crystallize, and an attempt to vacuum distill the product resulted only in charring it.

weight of $C_6H_5-\overset{H}{\underset{|}{C}}-O-CO-C_6H_5$ $C_6H_5-\underset{H}{\overset{|}{C}}-O-CO-C_6H_5$	7 grams
weight of C_6H_5COOH	2.5 grams
weight of resinous material	4 grams

Phenyl Brom Methyl Benzoate and Zinc.

36 grams of phenyl brom methyl benzoate were dissolved in 400 cc. of absolute ether and 48 grams of zinc dust were added in five gram portions. A thermometer was suspended in the flask so that the temperature of the reaction mixture could be kept at 20-25° throughout the reaction. During the time necessary to add all the zinc (about an hour) the mixture was kept well shaken. The material was then allowed to stand for four hours with only occasional shaking. During the reaction most of the ether had evaporated, so that

practically all of the dibenzoate had precipitated out on the zinc since it is quite insoluble in ether. After filtering the solution, the zinc was extracted twice with ether and twice with hot benzene and the extraction solvents were evaporated separately in vacuo. Three grams of $C_6H_5-\underset{H}{\underset{|}{C}}-O-CO-C_6H_5$ were obtained.

$$C_6H_5-\underset{H}{\underset{|}{C}}-O-CO-C_6H_5$$

On evaporation of the original ether solution, a tar was obtained which yielded 5 grams of benzoic acid when extracted with 50% alcohol. The resin which remained became very hard and brittle on standing. This material was powdered, and attempts were made to crystallize it from alcohol, ether, benzene, and glacial acetic acid, but all were unsuccessful, as the material always separated as a stringy mass, which became hard and brittle again on standing.

weight of $C_6H_5-\underset{H}{\underset{|}{C}}-O-CO-C_6H_5$ 3 grams.

$$C_6H_5-\underset{H}{\underset{|}{C}}-O-CO-C_6H_5$$

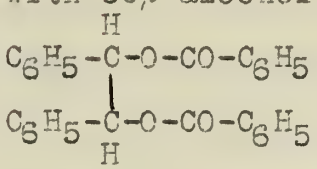
weight of C_6H_5COOH 5 grams.

weight of tar 10 grams.

Phenyl Brom Methyl Benzoate and Zinc.

To a solution of 47 grams of phenyl brom methyl benzoate in 800 cc. of benzene, were added 65 grams of zinc dust in three portions. During this time the mixture was kept well shaken up. The solution turned dark within a few minutes and the temperature rose about 10° for a period of half an hour. The mixture was heated on a steam cone for an hour and filtered hot. The zinc was extracted four times with hot benzene, and the extraction solutions were added to the original benzene solution and the whole concentrated to a volume of 50 cc. The thick, viscous mass so obtained was treated with 250 cc. of dry ether and filtered. The residue on the filter

paper, after crystallization from benzene melted at 246-247°. The gummy residue left after evaporation of the ether yielded benzoic acid when extracted with 50% alcohol.

weight of  1 gram.

weight of C_6H_5COOH 10 grams

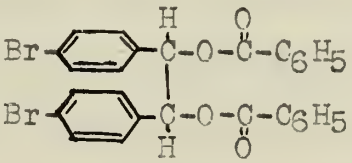
weight of tar 6 grams

Para Brom Phenyl Brom Methyl Benzoate and Zinc.

The para brom phenyl brom methyl benzoate was prepared by mixing equimolecular amounts of para brom benzaldehyde and benzoyl bromide and recrystallizing the product from petrol ether. (B.P.60-70°).

15 grams of the para brom phenyl brom methyl benzoate were dissolved in 200 cc. of absolute ether and 20 grams of zinc dust were added in three portions. The mixture was kept well shaken for an hour and then refluxed for four hours after which the solution was filtered and the ether evaporated in vacuo. After recrystallization of the solid product thus obtained from benzene, it was analyzed. M.P. of the substance 225°.

The zinc was extracted three times with hot benzene and the benzene solution distilled in vacuo. There was no product obtained in this way.

weight of  2 grams. 16.8% yield

Analysis: weight of subst. .0572

weight of AgBr .0368

%Br calc. for $C_{28}H_{20}O_4Br_2$ 27.58

%Br found 27.37

Meta Nitro Phenyl Brom Methyl Benzoate and Zinc.

The meta nitro phenyl brom methyl benzoate was prepared by mixing equimolecular amounts of meta nitro benzaldehyde and benzoyl bromide, and recrystallizing the product from petrol ether.

To an absolute ether solution of 30 grams of meta nitro phenyl brom methyl benzoate were added 30 grams of zinc dust in two portions, keeping the mixture well shaken meanwhile. The mixture was then refluxed for three hours, and filtered. The ether solution was concentrated in vacuo and a mass of crystals were obtained. These proved to be unchanged meta nitro phenyl brom methyl benzoate.

Phenyl Brom Methyl Benzoate and Copper Powder.

The copper powder was prepared by adding zinc dust to a solution of copper sulfate. After standing over night the copper was filtered off and digested with concentrated hydrochloric acid to remove all the zinc. Then the copper was washed with water till the washings gave no test for the chloride ion, after which it was washed with alcohol and ether and dried in a sulfuric acid dessicator.

39 grams of phenyl brom methyl benzoate were dissolved in 300 cc. of dry ether and 50 grams of copper powder were added in three portions, during a period of one-half hour. The mixture was kept well shaken during the addition, after which it was refluxed for 3½ hours. The copper was filtered off and extracted several times with hot benzene, and the benzene and ether solutions were concentrated in vacuo, separately, to a volume of 50 cc. each, and filtered. The solid material thus obtained, after crystallization from benzene, melted at 247°. The ether solution was evaporated to dryness and the tarry residue yielded benzoic acid when extracted with sodium hydroxide solution.

weight of $C_6H_5-\underset{H}{C}-O-CO-C_6H_5$ (with $C_6H_5-\underset{H}{C}-O-CO-C_6H_5$ on the branch) — 6 grams

weight of C_6H_5COOH — 2.5 grams

weight of tar — 5 grams

Phenyl Brom Methyl Benzoate and Sodium.

20 grams of phenyl brom methyl benzoate were dissolved in 300 cc. of dry ether and 2 grams of sodium in small, freshly cut flakes, were added in the course of two hours. The sodium became coated over quite rapidly so that fresh additions had to be made from time to time. The material was kept gently boiling on a steam cone for twenty-four hours, by which time a small amount of a white precipitate had formed. After filtering the solution, the ether was evaporated to a small volume and filtered. A few milligrams of $C_6H_5-\underset{H}{C}-O-COC_6H_5$ ($C_6H_5-\underset{H}{C}-O-COC_6H_5$) were obtained. The material was too small in amount to purify, but the crude material gave the melting point of 300-310°. The filtrate yielded only the usual resinous matter.

Phenyl Brom Methyl Benzoate and Magnesium.

To a solution of 42 grams of phenyl brom methyl benzoate in 300 cc. of absolute ether were added 25 grams of magnesium powder in three portions, during a period of half an hour. Apparently there was no reaction os a crystal of iodine was added and the material refluxed for 2½ hours. The ether was evaporated in vacuo and a melting point of the solid thus obtained was taken. It proved to be unchanged phenyl brom methyl benzoate.

Weight of the recovered product- 32 grams.

The 32 grams of phenyl brom methyl benzoate from the preceeding reaction, were dissolved in 300 cc. of dry ether and 10

grams of magnesium shavings and a crystal of iodine were added. The mixture was refluxed for seven hours, by which time a small amount of a white solid had separated. The solution was filtered and the magnesium was extracted with hot benzene. The benzene and ether solutions were concentrated separately to 50 cc. each, and the solid material which separated filtered off. It proved to be unchanged phenyl brom methyl benzoate. On evaporation of the benzene solution to dryness a black tarry mass was obtained, which on extraction with sodium hydroxide solution, yielded benzoic acid.

weight of recovered $C_6H_5-\underset{\underset{Br}{|}}{\overset{\overset{H}{|}}{C}}-O-CO.C_6H_5$ 8 grams

weight of C_6H_5COOH 2 grams

Phenyl Brom Methyl Benzoate and Aluminum.

41 grams of phenyl brom methyl benzoate were dissolved in 300 cc. of dry ether and 21 grams of aluminum powder were added in small portions. This addition required about half an hour. Within a few minutes after the first addition a small white precipitate was observed, but there was no noticeable evolution of heat. The solution colored gradually till it became dark red. After one and one-half hours, during which the mixture was kept well shaken, the aluminum was filtered off and the ether evaporated in vacuo. The solid which separated proved to be unchanged phenyl brom methyl benzoate. This was redissolved in 300 cc. of dry ether and the aluminum, together with six grams of fresh aluminum, was added, and the mixture refluxed for four hours. After filtering, the aluminum was extracted with hot benzene, and the two solutions were evaporated separately, in vacuo. Nothing separated out until the solutions were evaporated to dryness, when a black, gummy material was obtained. On extraction with petrol ether, this resinous substance yield-

ed benzoic acid, and an insoluble tar.

weight of C_6H_5COOH	9 grams
weight of tar	4 grams

Reduction of Phenyl Brom Methyl Benzoate with Aluminum Amalgam.

An excess of aluminum amalgam was added to a solution of 30 grams of phenyl brom methyl benzoate in 200 cc. of absolute ether to which 50 cc. of ordinary ether had been added. The amalgam became coated quite rapidly, and fresh amalgam had to be added from time to time. After about six hours the solution was filtered and the ether evaporated. The oil thus obtained was fracticnated in vacuo. The lower boiling fraction was redistilled under ordinary pressure and proved to be benzaldehyde, B.P. 175-180°.

The higher boiling fraction solidified and proved to be benzoic acid, M.P. 120-121°.

weight of benzaldehyde	5 grams
weight of benzoic acid	2 grams

VI. REACTION OF PHENYL BROM METHYL BENZOATE WITH SODIUM AND POTASSIUM CYANIDES.

Phenyl Brom Methyl Benzoate and Sodium Cyanide.

A petrol ether solution of 14 grams (1 mole) of phenyl brom methyl benzoate and a water solution of 4.7 grams (2 moles) of sodium cyanide were put in a bottle together and shaken for 20 hours. By that time a considerable amount of a dark red, stringy material had separated. This was filtered off and the two solutions separated. On evaporation of the petrol ether solution, in vacuo, a white solid was obtained which proved to be benzoic acid.

Weight of C_6H_5COOH	8 grams

Phenyl Brom Methyl Benzoate and Potassium Cyanide.

To a water solution of 2.3 grams of potassium cyanide were added in three portions, 10 grams of phenyl brom methyl benzoate. This mixture was shaken vigorously for several minutes when it suddenly began to react with the evolution of a considerable amount of heat. When cold, the mixture was extracted with ether, and an evaporation of the ether benzoic acid (M.P. 120°) was obtained.

The experiment was repeated, using the same amounts of material, but keeping the temperature down by means of an ice bath. After about twenty minutes, during which time the mixture had been shaken vigorously, the contents of the flask were extracted with ether. Benzoic acid was the only product obtained from the extraction. On acidification of the water solution, a small amount of benzoic acid was obtained.

Weight of C_6H_5COOH 4 grams

Phenyl Brom Methyl Benzoate and Potassium Cyanide.

10 grams of phenyl brom methyl benzoate were added in two portions to a solution of 2.3 grams of potassium cyanide in 10 cc. of water. After shaking vigorously for fifteen minutes, during which time the temperature was kept down by means of an ice bath, the contents of the flask were extracted with ether. On evaporation of the ether, only benzoic acid was obtained. M.P. 119-120°.

Phenyl Brom Methyl Benzoate and Potassium Cyanide.

A solution of 14 grams of phenyl brom methyl benzoate in 500 cc. of petrol ether and one of 6.2 grams of potassium cyanide in 200 cc. of water were placed in a bottle together and shaken in a shaking machine for 3½ hours. The small amount of sediment that had separated was filtered off, and the two solutions separated. The

solid material obtained by evaporation of the petrol ether in vacuo, proved to be unchanged phenyl brom methyl benzoate.

Weight of recovered phenyl brom methyl benzoate- 10 grams.

Phenyl Brom Methyl Benzoate and Potassium Cyanide.

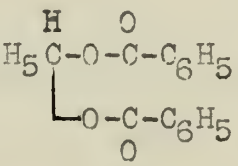
8 grams of potassium cyanide were dissolved in 50 cc. of water and 14 grams of phenyl brom methyl benzoate were dissolved in 150 cc. of alcohol free ether, and the two solutions were shaken together in a shaking machine for 3½ hours. The two layers were separated and the ether layer evaporated. Only benzoic acid was obtained. M.P. 120-121°.

VII. REACTION OF PHENYL BROM METHYL BENZOATE-PYRIDINE AND TRIMETHYL AMINE ADDITION PRODUCTS WITH BENZOIC ACID.

Phenyl Brom Methyl Benzoate-Pyridine Addition Compound and Benzoic Acid.

7 grams of the addition compound and 3.3 grams of benzoic acid were mixed, without solvent, in an Erlenmeyer flask and heated for 8 hours on a steam cone, at which temperature the mixture was fused. The oil thus obtained was allowed to stand over night when it was washed with water and 5% NaOH. The residue was recrystallized from petrol ether, and was found to be the dibenzoate of benzaldehyde. M.P. 59-60°.

The NaOH solution yielded 1 gram of C_6H_5COOH on acidification.

Yield of  .5 gram.

Phenyl Brom Methyl Benzoate-Pyridine Addition Compound and Benzoic Acid.

25 grams of the addition compound and 8.2 grams of benzoic

acid were mixed without solvent, in a round bottomed flask, which was stoppered and equipped with a calcium chloride tube and a thermometer, the bulb of which dipped below the surface of the mixture. The mixture was then heated on an oil bath kept at 140°. Complete fusion of the material took place below 100°, but at 125°, it suddenly deposited a considerable amount of solid material. The heating was continued for three hours altogether. When cold, the semi solid material was extracted with dry ether. The ether extract was washed with dilute sodium carbonate solution and 4 grams of benzoic acid (M.P. 119°) were obtained. The oil obtained by evaporation of the ether was fractionated and benzaldehyde (B.P. 175-180°) and a high-boiling liquid were obtained. On standing, this high-boiling fraction solidified, and proved to be the dibenzoate of benzaldehyde, (M.P. 60-61°).

The solid material which separated from the reaction mixture proved to be pyridine hydrobromide.

weight of C_6H_5COOH	4 grams
weight of C_6H_5CHO	3 grams
weight of $C_6H_5-\overset{H}{C}(O-CO-C_6H_5)_2$	2 grams

Phenyl Brom Methyl Benzoate-Trimethyl.Amine Addition Compound and Benzoic Acid.

A mixture of 5 grams of the addition compound and an equimolecular amount of benzoic acid were heated on a steam cone (at which temperature the mixture was fused) for twenty-four hours. After cooling, the material was extracted with dilute sodium hydroxide solution, washed with water, and recrystallized from petrol ether. The substance thus obtained proved to be benzaldehyde dibenzoate (M.P. 61-62°).

Weight of Product- 1 gram.

VIII. REACTION OF PHENYL BROM METHYL BENZOATE WITH POTASSIUM HYDROXIDE AND ALKALI SALTS OF ORGANIC ACIDS.

Phenyl Brom Methyl Benzoate and Potassium Hydroxide.

10 grams of phenyl brom methyl benzoate were dissolved in 150 cc. of absolute ether and an absolute ether suspension of 10 grams of powdered potassium hydroxide was added. The mixture was shaken at intervals for two hours and allowed to stand over night. After filtering, the ether was evaporated and the oil thus obtained was distilled. It proved to be benzaldehyde (B.P. 177-180°).

The white solid that had been filtered off was dissolved in water, and on acidification with hydrochloric acid, benzoic acid was precipitated (M.P. 120-121°).

weight of C_6H_5CHO	3 grams
weight of C_6H_5COOH	4 grams

Phenyl Brom Methyl Benzoate and Potassium Benzoate.

10 grams of phenyl brom methyl benzoate were dissolved in absolute ether and an absolute ether suspension of one mole of potassium benzoate was added. The mixture was shaken at intervals for three hours and allowed to stand over night. The solid was filtered off and the ether evaporated, but only phenyl brom methyl benzoate was obtained.

Phenyl Brom Methyl Benzoate and Potassium Benzoate.

2.7 grams of potassium benzoate were dissolved in as small an amount of water as possible and 5 grams of phenyl brom methyl benzoate were added. The mixture was well shaken and allowed to stand for six hours. The contents of the flask were extracted with ether and the ether solution evaporated to dryness. A solid, smell-

ing strongly of benzaldehyde was obtained, and was found to melt at 115-120°. This material was extracted with dilute sodium carbonate solution and the insoluble oil removed with ether. The alkaline solution yielded 4 grams of benzoic acid, and the oil from the ether solution gave a pure white sodium bisulfite addition compound, proving it to be benzaldehyde.

Phenyl Brom Methyl Benzoate and Sodium Acetate.

To a solution of 1.4 grams of sodium acetate in a very small amount of water were added five grams of phenyl brom methyl benzoate. After shaking the mixture thoroughly, it was allowed to stand for six hours, when it was extracted with ether and the ether solution evaporated. The solid thus obtained melted at 110-118° and smelled strongly of benzaldehyde. It was treated with dilute sodium carbonate solution and the insoluble oil removed with ether. The alkaline solution yielded 3 grams of benzoic acid. On evaporation of the ether an oil was obtained which gave a pure white, solid, sodium bisulfite addition compound, showing it to be benzaldehyde.

V. SUMMARY

The addition of aromatic acid halides to aromatic aldehydes is a general reaction, as shown by the large number of condensation products which have been prepared from both substituted and unsubstituted acid halides and aldehydes. As a rule the products formed from acid bromides are solid substances, although in some cases, particularly when positive substituents are present in the molecule, oils are formed. These oils can be shown to be the simple addition product, for on treatment with pyridine an addition reaction takes place which is characteristic of the acid halide-aldehyde addition compounds.

The addition takes place much more readily in the aromatic than in the alifatic series. In the former case, the substances react at room temperature, while in the latter series it is necessary to reflux the materials. Fused zinc chloride has been found efficient in catalyzing many of the reactions in both series. Substituting groups exert a decided influence upon the ease with which individual members react as well as upon the stability of the products formed. Thus, negative substituents tend to retard the speed of reaction, and usually produce more stable substances, while positive substituents hasten the reaction, and the products are more unstable. Acid chlorides react slower than acid bromides, and show a greater tendency to form oils. The reactions of acid chlorides are also characterized by a tendency to form semi-solid products from which unchanged acid chloride and aldehyde can be extracted.

The structure of the substances formed from the action of aromatic acid halides on aromatic aldehydes was shown by Adams and Volwiler[23] to be a simple addition of the acid halide to the

aldehyde carbonyl group, the halogen going to the aldehyde carbon.

The acid halide-aldehyde addition compounds show two types of reactions, in some cases acting as a mixture of acid halide and aldehyde, and in others the reaction is characteristic of the addition product. Thus, with primary and secondary alifatic amines, the benzoyl bromide-benzaldehyde addition compound behaves as a simple mixture, producing substituted benzamides, benzaldehyde and the amine hydrobromide. With tertiary alifatic amines and pyridine, addition products are formed.

With primary aromatic amines, benzoic acid and benzylidene anilines are formed, while secondary and tertiary aromatic amines produce dyes of the triphenyl methane series.

Concentrated aqueous solutions of potassium cyanide, potassium benzoate, potassium acetate, and potassium hydroxide completely hydrolyze the addition compound. Aluminium amalgam in moist ether also decomposes the phenyl brom methyl benzoate with the formation of benzaldehyde and benzoic acid.

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VII. V I T A

The writer of this thesis was born in Ireton, Iowa, November 13, 1889. He attended the grade schools at that place, but received his high school education in Sioux City, Iowa. In September, 1910, he entered Morningside College, from which he graduated with the degree of Bachelor of Arts, in June, 1915. During the summer of 1915, he attended the University of Chicago, taking work in the Department of Chemistry, and in September of the same year, he took up graduate work in Chemistry at the University of Illinois. He received the degree of Master of Arts from that Institution in June, 1917. During the time from February, 1916, to June, 1920, he has held the position of Assistant in Chemistry at the University of Illinois.

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